

AMENDED SPECIFICATION

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PATENT SPECIFICATION

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Improvements in or relating to Hair Fixing Resin Compositions

We, NATIONAL STARCH AND CHEMICAL CORPORATION, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 750 Third Avenue, City and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to film forming copolymer compositions which, because of their solubility and film-forming properties are ideally suited for use as the resin base of hair fixing formulations.

In order to be highly effective in hair fixing compositions such as aerosol hair sprays and hair setting lotions, the film-forming polymeric binders utilized therein as well as the films derived therefrom must meet a rigid set of requirements. Thus, the binders used in such formulations should be soluble in anhydrous organic solvents, yet the films cast from such hair fixing formulations should, ordinarily, either be water soluble or water dispersible in order to facilitate their easy removal from the user's hair. As is readily visualized, this is an unusual combination of properties which is further complicated by the requirement that the binder used in such formulations be completely compatible with the solvents and/or propellants ordinarily employed therein. Furthermore, the binders used should show little

or no tendency to interact with the perfumes or other optional ingredients utilized in hair fixing formulations.

In addition, the films cast from either aqueous or organic solvent solutions of these binders should be flexible and should simultaneously exhibit sufficient strength and elasticity; they should exhibit good adhesion to hair so as to avoid the occurrence of dusting or flaking when the hair is subjected to varying stresses; they should readily allow the hair to be recombined; they should maintain a non-tacky state despite humid conditions; they should be clear, transparent and glossy and should possess good anti-static properties; and, they should be easily removable by the use of water and/or soap or shampoo.

Needless to say, many polymeric systems have been utilized in an attempt to meet these stringent requirements. Among these are included: polyvinylpyrrolidone, copolymers of N-vinyl pyrrolidone with vinyl acetate, 5-5'-dimethyl hydantoinformaldehyde resins, copolymers of methyl vinyl ethers and maleic half esters, and terpolymers of N-vinyl pyrrolidone, an acrylate ester and acrylic acid, etc. Though each of the latter systems has met at least some of the above cited requirements, none has exhibited all of these requirements to an optimum degree.

Furthermore, each of British Patent No. 856,403 and 941,732 discloses a neutralized vinyl acetate-crotonic acid copolymer which is

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also applicable for use as a binder in hair fixing formulations. Although such polymeric binders exhibit many of the required properties specified hereinabove, and are superior in performance to many of the prior art binder systems, they are, nevertheless, deficient in certain solubility characteristics. Thus, they do not exhibit the broad range of solubility in aqueous and non-aqueous systems which will enable them to be readily stored at high concentration levels and, thereafter, formulated at relatively low concentrations. This deficiency in their solubility characteristics also limits the utility of these resins when they are sought to be utilized in alcohol-water based wave set lotions as well as in alcohol based aerosol hair sprays. With regard to the latter hair sprays, the neutralized vinyl acetate-crotonic acid copolymers exhibit limited compatibility with the hydrocarbon propellants present therein. Additionally, since these vinyl acetate-crotonic acid copolymers are most frequently utilized when they have been neutralized, the films derived therefrom are water sensitive and thereby provide a reduced degree of holding power to the hair.

It is thus the prime object of this invention to improve upon the performance which is displayed by vinyl acetate-crotonic acid copolymeric binders when present in hair fixing formulations. More specifically, it is the prime object of this invention to provide film-forming polymers for use, as binders, in hair fixing formulations, said polymers exhibiting most or all of the above described properties required in such binders and being particularly characterized by their solubility in both aqueous and organic solvents as well as by their compatibility with the hydrocarbons commonly used as aerosol propellants.

We have now discovered that all of the previously described requirements for an effective hair fixing formulation are met by utilizing the novel class of copolymers herein-after described as the film forming binder component of the hair fixing compositions of this invention. Particularly significant are the broadened solubility and compatibility characteristics exhibited by these novel binders. Thus, for example, they display a greater degree of solubility in the organic solvents typically used in aerosol hair sprays as well as in the aqueous solvent systems typically utilized in wave set lotions. In addition, they exhibit greater compatibility with the hydrocarbon propellants typically used in aerosol hair sprays. Furthermore, if neutralization of these resins is desired by the practitioner, the lower levels of neutralization that can be used insure the deposition, onto the hair, of films having a minimal degree of water sensitivity which, although they are readily removable by washing, provide a greater degree of holding power and thereby enable the thus treated hair to retain its shape and body. It should also be

noted that the preferred class of the copolymer binders of this invention are not plasticized as a result of the polymerization procedure utilized for their preparation.

The film forming terpolymers utilizable as binders in the hair fixing formulations of this invention comprise copolymers derived from vinyl acetate, crotonic acid, and at least one vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid having from 5 to 10 carbon atoms in the carboxylic acid moiety, said acid having the formula



wherein R_1 and R_2 are alkyl radicals and R_3 is a radical selected from the group consisting of hydrogen, alkyl and aryl radicals. By alpha-branched, we refer to the presence of at least one branch emanating from the carbon atom immediately adjacent to the carboxyl group, such branching being represented by either the R_1 or R_2 radicals in the above described formula. It is the addition of the moieties derived from the latter class of vinyl esters to the prior art vinyl acetate-crotonic acid copolymers which is primarily responsible for providing the resulting polymeric binders with their improved solubility and compatibility characteristics.

It should be noted that one may employ as the extra monomeric component a mixture of more than one of these vinyl esters of alpha-branched saturated aliphatic monocarboxylic acids having from 5 to 10 carbon atoms in the carboxylic acid moiety, the latter acids of the type set forth hereinabove. A preferred mixture of this type consists of the vinyl esters of a mixture containing 56%, by weight, of 2,2,4,4 - tetramethyl valeric acid and 27%, by weight, of 2 - isopropyl - 2,3 - dimethyl butyric acid with the remaining acid components comprising isomers of the acids. For purposes of brevity, the latter monomer mixture, which contains only vinyl esters of nine carbon atom acids, will be hereinafter referred to as "monomeric mixture A."

In order to provide binders which will function particularly efficiently in the novel hair fixing compositions of this invention, it is desirable that the resulting co-polymer contains from 7 to 89% of vinyl acetate, from 6 to 13% of crotonic acid and from 5 to 80% of the selected vinyl ester; the percentages all being based on the total weight of the copolymer.

As for the actual preparation of these polymeric film forming binders, they must be made by a procedure which will provide the terpolymer in the form of solid beads, known in the art as "pearls". Thus, they may be pre-

pared by means of free radical initiated processes utilizing bulk, suspension or solution polymerization techniques. Solution polymerization of the comonomers, followed by the step of dispersing the solution of the copolymer in water to convert the copolymer into relatively large particles, known as beads or pearls, which are easily separated, washed and dried is preferred, however, because of the convenient physical form of the resulting copolymer. In any event, the polymeric beads, whether prepared by means of bulk suspension or solution polymerization techniques, are all characterized by their bead form and their solubility in both aqueous and organic solvents as well as by their compatibility with aerosol propellants.

It should be noted that the latter copolymers may be partially neutralized prior to their being incorporated into the ultimate hair fixing formulation thus permitting them to be removed from the hair merely by rinsing with water. This may be accomplished by reacting the terpolymer with a concentration of an alkaline reagent which is equivalent on a molar basis to no more than 80% of the available carboxyl groups present on the terpolymer. Neutralization to an extent greater than 80% renders the ultimate composition unsuitable for hair fixing purposes. Applicable alkaline materials which may be utilized in this manner include: sodium and potassium hydroxide; ammonia; primary, secondary and tertiary amines; alkanolamines; and, hydroxyamines such as 2-amino-2-methyl-1,3-propanediol. However, if such terpolymers are not neutralized, in this manner, their eventual removal may still be readily affected by the application of weak alkaline aqueous solution, e.g., soap and water.

The present invention provides a hair-fixing composition comprising a solution of the beads in a solvent selected from an organic solvent and a mixture of an organic solvent and water.

In utilizing the above described polymeric binders in the preparation of aerosol hair sprays, the other essential ingredients which must be admixed therewith are a solvent and a propellant, although in some instances the propellant will serve both the latter functions. The preferred solvents are alcohols such as ethanol and isopropanol. In addition to their solubility properties, the prime advantages of these solvents are their ability to dry quickly, their minimal effect on the metal containers ordinarily utilized for these pressurized aerosol formulations and their accepted use in cosmetic applications. Other solvents which may be used include methylene chloride and 1,1,1-trichloroethane, etc.

Various types of aerosol propellants are well known to those skilled in the art. Thus the commonly used propellants include trichlorofluoromethane, dichlorodifluoromethane, isobutane and propane, etc., as well as mixtures

of the latter propellants. These propellants are readily compatible with the binder-solvent solutions utilized in this invention.

In general, the method for preparing the hair spray formulations of this invention merely involves dissolving the copolymer beads in the selected solvent, adding any modifying agents whose presence may be desired, and thereupon combining the resulting solution with the selected aerosol propellant.

Thus, it may be noted that the novel hair spray formulations of this invention will in all cases contain at least three essential components. The first of the latter components will be what may be termed as the active ingredient comprising one or more of the above described copolymers which serves as the binder for the formulation. Secondly, there will be one or more solvents which serve as vehicles for the binder. And, finally, there is the propellant which serves to effect the discharge of the aforesaid binder and vehicle from the container wherein the formulation is packaged.

With regard to proportions, the final hair spray formulations typically contain the polymeric binder in a concentration ranging from 0.5 to 7% by weight; the solvent in a concentration ranging from 8 to 90% by weight; and, the propellant in a concentration ranging from 10 to 85% by weight. The latter proportions should, however, be considered as being merely illustrative inasmuch as it may well be possible to prepare operable formulations having concentrations of components which fall outside the above suggested ranges.

In addition, it should be noted that the copolymer beads are equally as effective when utilized in aqueous or alcoholic hair setting lotions. Such lotions may be directly applied to the hair or they may be sprayed thereon utilizing conventional spray nozzles. The application of such lotions may take place prior to, during, or after the desired hair style has been achieved.

The latter hair lotions are prepared by merely admixing the copolymer beads with the selected solvent, such solvents usually comprising a mixture, with water, of an alcohol such as ethanol or isopropanol. With regard to proportions, the lotions typically contain from 0.5 to 7% by weight, of the polymeric binder, while any desired ratio of alcohol to water in the solvent system may be utilized therein.

Optional additives may be incorporated into the hair fixing formulations of this invention in order to modify certain properties thereof. Among these additives may be included: plasticizers such as glycols, phthalate esters and glycerine; silicones; emollients, lubricants and penetrants such as lanolin compounds, protein hydrolizates and other protein derivatives, ethylene oxide adducts, and polyoxyethylene cholesterol; dyes and other colorants; and, perfumes. As pre-

viously noted, the polymeric binders of this invention show little or no tendency to chemically interact with such additives.

- 5 The resulting hair fixing formulations exhibit all of the characteristics required of such a product. Their films are transparent, glossy, flexible, and strong. They possess good anti-static properties, adhere well to hair, are easily removed by soapy water or shampoos, allow the hair to be readily combed, do not yellow on aging, and do not become tacky when exposed to high humidities.

- 10 In the following examples, which further illustrate this invention, all parts given are by weight unless otherwise indicated. Example 1 merely describes the preparation of solid copolymer beads.

EXAMPLE I

- 20 This example illustrates a method for the polymerization of a typical copolymer applicable for use in the hair fixing formulations of this invention.

- 25 The initial reaction mixture consisted of 75.0 parts of vinyl acetate, 2.5 parts of crotonic acid, 15.0 parts of monomeric mixture A and 4 parts of benzoyl peroxide, the latter reagents being dissolved in 20 parts

of ethyl acetate. The solution was maintained at the reflux temperature whereupon 7.5 parts of crotonic acid were added. Ethyl acetate was also added, as required, in order to maintain a workable viscosity during the polymerization; the total amount of ethyl acetate thus introduced comprising 70 parts. At the completion of the polymerization reaction, the copolymer solution was dispersed, with agitation, in water containing 0.1% of polyvinyl alcohol, as based on the weight of the polymer solids, thereby converting the copolymer into the form of pearls. The ethyl acetate and any residual vinyl acetate monomer were then removed by distillation. The aqueous dispersion of the copolymer was then centrifuged to separate the copolymer pearls, which were washed and dried. The resulting copolymer will hereinafter be referred to as "copolymer No. 1".

Additional copolymers applicable for use in our hair fixing formulations were thereafter prepared by means of the procedure described hereinabove; the reagents and the concentrations in which they were used to prepare the respective copolymers being set forth in the following table:

| Reagents | parts Copolymer | | | | | | |
|---|--------------------|------|------|------|------|------|------|
| | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| vinyl acetate | 75.0 | 75.0 | 81.0 | 63.0 | 49.5 | 30.0 | 10.0 |
| crotonic acid | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| vinyl pivalate | 15.0 | — | — | — | — | — | — |
| a mixture of vinyl esters of alpha-branched saturated aliphatic monocarboxylic acids containing ten carbon atoms in the acid moiety | — | 15.0 | — | — | — | — | — |
| monomer mixture A | — | — | 9.0 | 27.0 | 40.5 | 60.0 | 80.0 |

EXAMPLE II

- 60 This example illustrates the improved performance characteristics exhibited by the copolymers utilized in the hair fixing formulations of this invention.

- 65 *Alcohol Solubility*—Anhydrous ethanol solutions containing respectively, 3 and 30%, by weight, of the copolymer composition whose complete preparation is described in Example I, hereinabove, and 3 and 30%, by weight, of a control polymer, i.e., a polymer consisting of 90 parts of vinyl acetate and 10 parts of crotonic acid, were prepared by admixing the required ingredients at 72°F. and subsequently

heating them to a temperature of 85°F. The resulting solutions were then cooled at a rate of 2°F./minute and observations made of the temperature at which the polymer first appeared to come out of solution, i.e., the "Cloud Point". A lower cloud point is thus indicative of greater solubility in the anhydrous ethanol which, it should be noted, is a typical aerosol solvent.

The results of the above determination, which clearly indicate the increased solubility of the copolymer of this invention in anhydrous ethanol, are presented in the following table:

| | Cloud Point (°F.) | |
|-----------------|-------------------|----|
| control | 82 | 68 |
| copolymer No. 1 | 58 | 38 |

- 15 The improved alcohol solubility of the novel copolymers employed in the products of this invention was further illustrated by the preparation, at a temperature of 77°C., of 3% by weight, anhydrous ethanol solutions of a variety of the copolymers of this invention. Acceptable solubility properties were indicated by the resulting appearance, after about 20 minutes of agitation, of clear or relatively clear solutions which were free of insolubles. The resulting data is presented in the following table: 10

| Copolymer | Alcohol stability |
|------------------------------|-------------------|
| control | cloudy |
| copolymer No. 1 of Example I | clear |
| copolymer No. 2 of Example I | clear |
| copolymer No. 3 of Example I | clear |
| copolymer No. 4 of Example I | clear |
| copolymer No. 5 of Example I | clear |
| copolymer No. 6 of Example I | clear |
| copolymer No. 7 of Example I | clear |
| copolymer No. 8 of Example I | clear |

- 15 *Water Solubility* — The copolymers utilized in this test procedure were initially neutralized with 2 - amino - 2 - methyl - 1,3-propanediol to the extent of 60% of the theoretical equimolar amount of carboxylic acid groups present in the copolymer. Thereafter, 2 parts of a 30%, by weight, anhydrous ethanol solution of the neutralized copolymer were diluted with 18 parts of water and observations made as to the clarity of the resulting solution. 20 to a similar sample, comprising 2 parts of a 30%, by weight, anhydrous ethanol solution of the neutralized copolymer. Observations were made as to the amount of water thus required to produce turbidity in the solution. Since the addition of 18 parts of water without a significant change in clarity is sufficient to indicate excellent water solubility, all the samples that remained clear after the addition of 18 parts of water were removed from the test and assigned a value of ">18". 30 35

In addition, small portions of water, amounting to one part in each instance, were added

The results of these tests are set forth in the following table: 40

| copolymer | parts of water to turbidity | appearance of totally diluted polymer sol'n |
|------------------------------|--------------------------------|---|
| control | 2.6 | cloudy |
| copolymer No. 1 of Example I | >18 | clear |
| copolymer No. 4 of Example I | >18 | clear |
| copolymer No. 5 of Example I | >18 | clear |
| copolymer No. 6 of Example I | >18 | clear |
| copolymer No. 7 of Example I | >18 | clear |

5 The results summarized hereinabove clearly indicate the increased water solubility of the copolymers employed in the products of this invention.

10 *Propellant Compatibility* — The copolymers utilized in this test procedure were initially neutralized with 2 - amino - 2 - methyl-1,3 - propanediol to the extent of 80% of the theoretical equimolar amount of the carboxylic acid groups present in the terpolymer. Thereupon isobutane, a typical aerosol propellant,

was added in one part, by weight, increments to 15 parts of a 5.0%, by weight, anhydrous ethanol solution of the selected copolymer. When the point of turbidity was reached, the ratio of isobutane to ethanol was noted with higher values of isobutane indicating a greater degree of compatibility with the isobutane on the part of the copolymer.

The results of this test procedure are presented in the following table:

| copolymer | isobutane:ethanol ratio |
|------------------------------|-------------------------|
| control | 0.5:99.5 |
| copolymer No. 1 of Example I | 33:67 |
| copolymer No. 5 of Example I | 46:54 |
| copolymer No. 6 of Example I | 54:46 |
| copolymer No. 7 of Example I | 68:32 |
| copolymer No. 8 of Example I | >70:30 |

25 *Film Hardness* — A series of films having a wet thickness of 1.5 mils were cast on glass plates from 30%, by weight, solutions of the copolymers in anhydrous ethanol. These films were dried for 24 hours at a temperature of 72°F. and a relative humidity of 55%. The surface hardness of these films was then tested using a Sward Hardness Rocker. The

results of the hardness tests were rated on a numerical scale of from 0 to 100. Thus, a glass plate gives a value of 100, while a value of 0 implies a surface which is so soft as to be tacky.

The results of this test procedure are described in the following table:

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| copolymer | Sward Rocker Hardness |
|------------------------------|-----------------------|
| control | 30 |
| copolymer No. 1 of Example I | 26 |
| copolymer No. 2 of Example I | 26 |
| copolymer No. 5 of Example I | 26 |
| copolymer No. 6 of Example I | 28 |

The results presented hereinabove clearly indicate that the films derived from copolymers which contain the alpha-branched vinyl esters as the third or higher component therein, display a degree of hardness which is equivalent to the hardness exhibited by the films derived from copolymers of vinyl acetate and crotonic acid.

EXAMPLE III

This example illustrates the preparation of an aerosol hair spray formulation typical of the novel products of this invention utilizing the 75.0:10:15.0 vinyl acetate:crotonic acid: monomer mixture A copolymer, i.e., copolymer No. 1, whose preparation was described in Example I, hereinabove.

A solution consisting of 1.2 parts of the copolymer in 38.8 parts of anhydrous ethanol was prepared and subsequently introduced into an aerosol container which had been charged

with 60 parts of a 60:40 propellant mixture of trichlorofluoromethane and dichlorodifluoromethane to an internal pressure of 30 pounds per square inch gauge. It is to be noted that the resulting system was found to be completely compatible.

When utilized, the resulting hair spray deposited a film which was characterized by its clarity, gloss and flexibility. It served to hold the desired hair style in place while also allowing for its recombining. Of great significance was the fact that it was readily removed from the hair by the use of a conventional shampoo.

EXAMPLE IV

This example illustrates the preparation of a wave setting lotion typical of the products of this invention.

The following ingredients were charged into a reaction vessel equipped with means for mechanical agitation.

| | parts |
|--|-------|
| a 75.0 : 10:15.0 vinyl acetate:crotonic acid: monomer mixture A copolymer (as prepared in Example I) | 3.0 |
| 2-amino-2-methyl-1,3-propanediol | 0.3 |
| anhydrous ethanol | 14.7 |
| water | 82.0 |

The resulting clear solution which comprised the wave set lotion thus contained a polymeric binder which had been neutralized to the extent of 80% of the theoretical equimolar amount of carboxylic acid groups present in the copolymer.

When utilized, this wave setting lotion deposited a clear, glossy, flexible film which was readily removed from the hair by a thorough washing with water.

Summarizing, it is thus seen that this inven-

tion provides for the preparation of novel improved copolymer compositions which are ideally suited for use as the polymeric binder in a wide variety of hair fixing compositions.

WHAT WE CLAIM IS—

1. A hair fixing composition comprising a solution in a solvent selected from an organic solvent and a mixture of an organic solvent and water, of beads of a copolymer of vinyl acetate, crotonic acid and at least one vinyl ester of an alpha-branched saturated aliphatic mono-

carboxylic acid having from 5 to 10 carbon atoms in the carboxylic acid moiety, said acid having the formula



5 wherein R_1 and R_2 are alkyl radicals and R_3 is selected from hydrogen, alkyl and aryl radicals.

2. A composition according to claim 1, in which vinyl acetate is present in a concentration of from 7 to 89%, crotonic acid is present in a concentration of from 6 to 13%, and said vinyl ester is present in a concentration of from 5 to 80%; the percentages being based on the total weight of said copolymer.

15 3. A composition according to claim 1 or 2, wherein the copolymer has been neutralized with an alkaline reagent, in an amount equivalent on a molar basis to no more than 80% of the available carboxyl groups of said copolymer.

20 4. A composition according to any one of the preceding claims, in which the vinyl ester component is vinyl pivalate.

5. A composition according to Claim 1, 2 or 3, in which the vinyl ester component is a mixture of vinyl esters of 2,2,4,4 - tetramethyl valeric acid, 2 - isopropyl - 2,3 - dimethyl butyric acid and isomers thereof.

30 6. A composition according to any preceding claim, which further comprises a hydrocarbon aerosol propellant.

7. A process for the preparation of a hair fixing composition, said process comprising making solid copolymer beads by polymerizing, in the presence of free radical initiators: (1) vinyl acetate; (2) crotonic acid; and, (3) at least one vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid having from 5 to 10 carbon atoms in the carboxylic acid moiety, said acid having the formula



wherein R_1 and R_2 are alkyl radicals and R_3

is selected from hydrogen, alkyl and aryl radicals and dissolving said copolymer in an organic solvent or in a mixture of an organic solvent and water.

8. A process according to claim 7, in which vinyl acetate is present in a concentration of from 7 to 89%, crotonic acid is present in a concentration of from 6 to 13%, and said vinyl ester is present in a concentration of from 5 to 80%; the percentages being based on the total weight of said copolymer.

9. A process according to claim 7 or 8, in which the terpolymer resulting from the polymerization step is neutralized with an alkaline reagent in an amount equivalent to no more than 80% of the available carboxyl groups of said terpolymer.

10. A process according to Claim 7, 8 or 9, in which the vinyl ester component is vinyl pivalate.

11. A process according to Claim 7, 8, or 9, in which the vinyl ester component is a mixture of vinyl esters of 2,2,4,4 - tetramethyl valeric acid, 2 - isopropyl - 2,3 - dimethyl butyric acid and isomers thereof.

12. A process according to any one of claims 7 to 11, in which there is mixed with the dissolved copolymer a hydrocarbon aerosol propellant.

13. The process for the preparation of a composition as claimed in claim 1, substantially as hereinbefore described with reference to Example II, III or IV.

14. A composition whenever prepared by the process claimed in any one of claims 7 to 12.

15. A hair fixing composition according to claim 1, substantially as hereinbefore described with reference to Example II.

16. An aerosol hair spray formulation containing a composition according to claim 1, substantially as hereinbefore described with reference to Example III.

17. A wave setting lotion containing a composition according to claim 1, substantially as hereinbefore described with reference to Example IV.

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